

Chromium, Hexavalent, Dissolved: Solvent Extraction, AAS Method

Reference: EPA Method 218.4.

Introduction

Hexavalent chromium is a potential carcinogen; hence, its determination in potable water supplies is very important. Chromium salts are used extensively in industrial processes and may enter the water supply through the discharge of wastes. Chromium may exist in a water supply in both the hexavalent and the trivalent state, although the trivalent form rarely occurs in a potable water supply.

Principle

Hexavalent chromium is selectively chelated with APDC at pH 3.5 and extracted into MIBK and determined by atomic absorption spectrophotometry.

Scope

This method is applicable to all types of waters. The range is 0.001-0.200 mg/L Cr (hexavalent).

Apparatus and Materials

- A. Atomic absorption spectrophotometer.
- B. 200 mL volumetric flasks.
- C. Mechanical shaker.

Reagents

- A. Buffer solution: Dissolve 100 g ammonium acetate ($\text{CH}_3\text{COONH}_4$) in distilled deionized water (DDW) and add 40 mL of 30% (v/v) ammonium hydroxide per L. Adjust the pH to 3.4 with concentrated HNO_3 . Dilute to 2000 mL.

- B. APDC, 1%: Dissolve 1.0 g ammonium pyrrolidine dithiocarbamate in 100 mL DDW. Filter through 0.45 μ membrane filter before using. Prepare fresh daily.
- C. MIBK: Methyl isobutyl ketone, reagent grade.
- D. Indicator solution: Dissolve 0.050 g methyl red and 0.100 g bromophenol blue in 50 mL ethanol. Dilute to 100 mL with DDW.
- E. Stock Standard Chromium Solution (500 mg/L Cr^{+6}): Dissolve 1.415 g of anhydrous potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in DDW and dilute to 1 L in a volumetric flask.
- F. Intermediate Stock Standard Chromium Solution (5.00 mg/L Cr^{+6}): Dilute a 10 mL aliquot of stock Cr^{+6} solution to 1 L in a volumetric flask.
- G. Working Hexavalent Chromium Standards: Dilute the following aliquots of Intermediate Stock Chromium Standard to 1 L in a volumetric Flask.

<u>mL INTERMEDIATE STOCK STANDARD CHROMIUM SOLUTION</u>	<u>CONCENTRATION Cr^{+6} mg/L</u>
50.0	0.250
40.0	0.200
20.0	0.100
10.0	0.050
5.0	0.025

Sample Preparation

Samples should be filtered through a 0.45 μ membrane filter prior to analysis.

Procedure

- A. Pipette 100 mL of unacidified samples and standards into individual 200 mL volumetric flasks.
- B. Add 5 drops of indicator solution and titrate with 0.25N H_2SO_4 to a faint red color, pH 4.3.
- C. Add 5 mL buffer solution.

- D. Add 5 mL APDC, mix, and let stand 5 min.
- E. Add 16 mL MIBK and shake for 5 min on mechanical shaker. Let stand 10 min to allow separation of phases.
- F. Float MIBK to top of flask by carefully adding DDW.
- G. Analyze by atomic absorption according to following settings.

Instrumental Parameters

- | | | |
|----|--------------|------------------|
| A. | Wavelength | 357.9 nm |
| B. | Fuel/oxidant | Acetylene-Air |
| C. | Flame | Partial Reducing |

Interferences

Cobalt, iron, and nickel have been found to depress chromium absorbance but avoiding a very rich reducing flame minimizes this greatly.

Precision and Accuracy

- A. In a single laboratory (Alberta Pollution Control Laboratory) using a surface water, sewage, and an industrial effluent at concentrations of 0.016, 0.196, and 1.097 mg/L Cr⁺⁶, the coefficients of variation were 2.63%, 1.82%, and 0.75%, respectively.
- B. In a single laboratory (Alberta Pollution Control Laboratory) using a river water and a sewage effluent at concentrations of 0.016 and 0.196 mg/L Cr⁺⁶, the coefficients of variation were 100.0% and 97.7%, respectively.

Bibliography

Analytical Methods Manual, Water Quality Branch, Environment Canada, Ottawa. (1974).